

# Air Pollution Control in Municipal Solid Waste Incinerators

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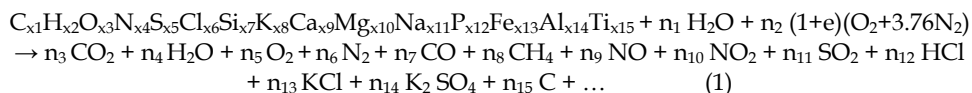
## 1. Introduction

Municipal solid waste (MSW) remains a major problem in modern societies, even though the significant efforts to prevent, reduce, reuse and recycle. At present, municipal solid waste incineration (MSWI) in waste-to-energy (WtE) plants is one of the main management options in most of the developed countries. The technology for recovering energy from MSW has evolved over the years and now sophisticated air pollution control (APC) equipment insures that emissions comply with the stringent limits established in developed countries. This chapter shows the role of incineration in WtE processes in the ambit of MSW management, giving an overview of the MSWI technologies and APC devices used for cleaning the gaseous emissions. The main focus is on the key air pollutants, such as dioxins and furans. At the end, the impact of emission on health risks is also briefly considered.

## 2. Contribution of MSWI in modern solid waste management systems

The waste hierarchy in force in European Union, Directive 2008/98/EC, and in other developed countries sets out the following options for waste management: prevention, reuse, recycling, other recovery (e.g. energy recovery) and disposal. Indeed, nowadays modern systems embrace in general different methodologies aiming as much as possible to achieve sustainable global solutions. Life Cycle Assessment (LCA) tools have been used to assess the potential environmental burdens of different waste management strategies, from environmental, energetic and economic point of view. These calculations have shown that landfilling, even if gas is recovered and leachate is collected and treated, should be avoided, due to the fact that resources in the waste are inefficiently utilised (Sundqvist, 2005). Environmental sound alternatives include incineration, material recycling, anaerobic digestion or composting.

Incineration is a combustion process at high temperature that allows rather complete oxidation of solid wastes, liquids or gases. Combustion systems may be very complex involving simultaneous coupled heat and mass transfer, chemical reaction and fluid flows. A global equation for representing combustion of wastes in air, may take the following form (Jenkins et al., 1998):



It is important to note that the empirical formula represented in Eq. (1) is incomplete since it includes only 15 elements and a real waste may contain a lot more, some of them found in traces; the molar indices  $x_1$  to  $x_{15}$  can vary widely;  $n_1$  corresponds to the moisture in waste;  $n_2$  is related with the amount of air (considered as a binary mixture of  $O_2$  and  $N_2$ ) used in the combustion;  $(1+e)$  is the excess of air in relation to the stoichiometric amount, usually ranges from 1.2 to 2.5 (depending on whether the fuel is gas, liquid or solid) (BREF, 2006);  $n_3$  to  $n_{15}$  correspond to the stoichiometric coefficients of the different species that can be found as reaction products, among many others that can be released in the emissions. If the incinerated material is represented by a simpler formula, like  $C_uH_vO_wN_xS_y$ , then the combustion equation may be simplified and represented by Eq. (2)



In the scope of thermal treatments of solid wastes, Fig. 1 shows the difference in terms of pyrolysis, gasification and incineration by taking into account the amount of air present.

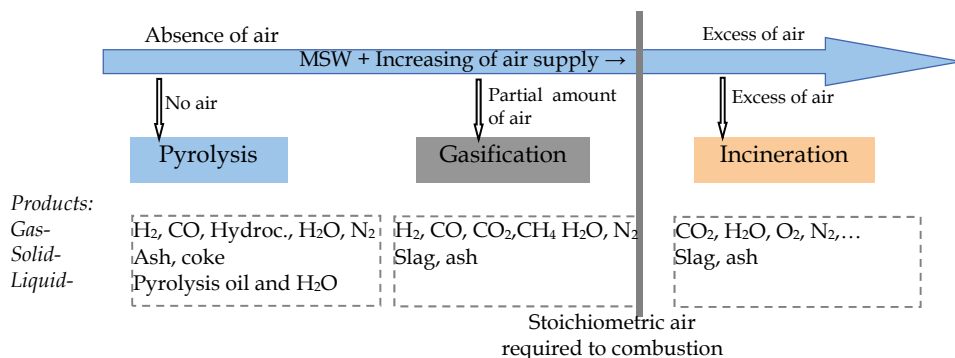


Fig. 1. Classification of the thermal technologies for treating MSW (based on DEFRA, 2007).

These thermal processes correspond to very different technologies in the way of treating waste and energy recovery. In incineration, the energy is released through the oxidation reactions, and its recovery occurs directly from the gases formed.

At present, municipal solid waste incineration (MSWI) in waste-to-energy (WtE) has confirmed to be an environmentally friendly solution and a common alternative to landfilling, while allowing recovery of a large part of the energy contained in MSW. In practice, MSWI has several advantages and disadvantages as reported in Table 1. Nevertheless, the main problems associated to these processes are probably the large volume of gaseous emissions which may pose environmental health risks (Moy et al., 2008) and hazardous solid wastes that remain after incineration as fly ash or air pollution control (APC) residues (Quina et al., 2008a,b).

MSW is generated by households and other similar wastes in nature and composition, which in general is collected and managed by or on behalf of municipal authorities, and

includes materials such as paper, plastics, food, glass and household appliances. Fig. 2 shows typical composition of MSW usually associated to these waste streams, based on Gentil et al. (2009), and information reported by environmental agencies from Portugal (APA) and from USA (EPA) for the reference year 2009.

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>- handle waste without pre-treatment</li> <li>- reduce landfilling demand for MSW</li> <li>- reduce waste volume by 90%</li> <li>- reduce waste weight by 70%</li> <li>- possibility of recovering energy (electricity or heat)</li> <li>- if well managed, low air pollution is released</li> <li>- destroy potential pathogens and toxic organic contaminants</li> <li>- can be located close to the centre of gravity of MSW generation</li> <li>- reduce cost of waste transportation</li> <li>- require minimum land</li> <li>- stack emissions are odour-free</li> <li>- reduce organic materials mainly to CO<sub>2</sub> instead CH<sub>4</sub> and other VOC</li> </ul>	<ul style="list-style-type: none"> <li>- originate hazardous waste (APC residues), that requires safe disposal</li> <li>- originate slags (bottom ashes)</li> <li>- originate huge volume of flue gases</li> <li>- high investment and operating costs</li> <li>- high maintenance costs</li> <li>- require skilled staff</li> <li>- require suitable composition for autocombustion</li> <li>- negative public perception (so far)</li> </ul>

Table 1. Advantages and disadvantages of municipal solid waste incineration.

According to Eurostat data for EU-27 State Members, MSW produced in 2008 was on average about 524 kg per capita, but it is possible to find values between 800 kg in Denmark to 300 kg in the Czech Republic (Eurostat 2010). Globally, in 2008, the EU-27 countries produced the huge amount of 259 Mt of MSW, whereas 221 Mt was accounted for in the EU-15. Figs. 3-4 depict the way that MSW stream has been treated in various countries, and in particular Fig. 3 shows the evolution in the EU-27 from 1995 to 2009 taken into account landfill, incineration, composting and recycling. It is important to note that, in 2009, about 20% of waste was incinerated, which correspond to 50.9 Mt. Considering that the average lower calorific value (LCV) should not be less than 7 MJ/kg of waste, in order to occur a chain of reactions able to self-supporting combustion, and assuming that in Europe the LCV

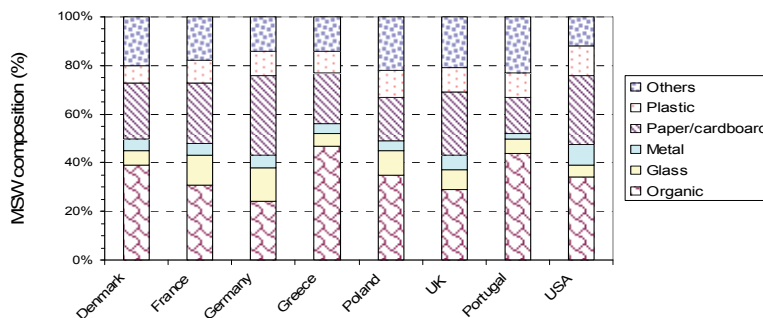


Fig. 2. Composition of MSW (based on Gentil et al., 2009, Portugal APA, US EPA).

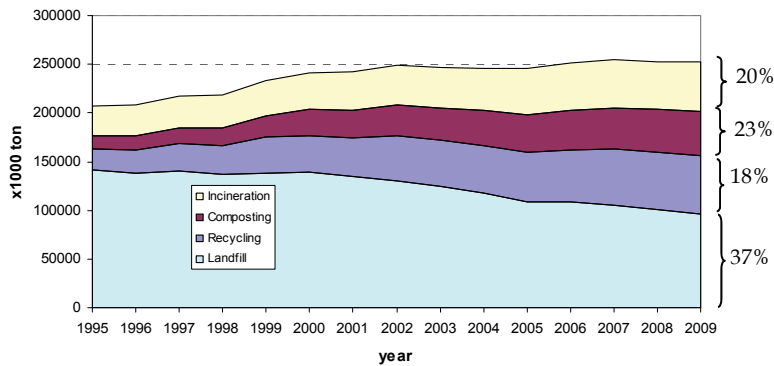


Fig. 3. Contribution of landfill, incineration, composting and recycling in EU-27 State Members (Source: based on Eurostat databases).

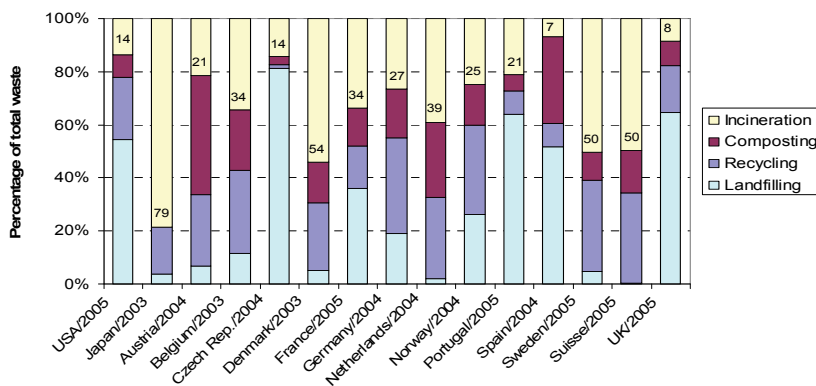


Fig. 4. Contrasting MSW management practice in selected countries, in landfills, incineration, composting and recycling (Source: based on OECD statistic databases).

is in the range of 9-13 MJ/kg (World Bank Report, 1999), the combustion of 50.9 Mt led to an enormous amount of energy available for recovery. Fig. 3 points out that landfilling has been gradually decreasing since 1995, and in 2009 its contribution accounts for 37%. According to Fig. 4, Japan is the country where incineration has higher contribution (79%) and in Europe, countries such as Denmark (54%) and Sweden (50%) have the highest rates. By taking into account the information from BREF (2006) for waste incineration, Table 2 summarizes the number and total capacity of the existing incinerators in 17 European countries.

It is important to note that these numbers may vary according to the source of information used, and the year of reference. According to DEFRA (2007), in 2000, about 291 incineration sites with energy recovery located in 18 Western European countries, processed about 50

Country	Number of MSWI	Capacity Mt/year	Country	Number of MSWI	Capacity Mt/year
Austria	5	0.5	Luxembourg	1	0.15
Belgium	17	2.4	Portugal	3	1.2
Denmark	32	2.7	Spain	9	1.1
Finland	1	0.07	Sweden	30	2.5
France	210	11.7	Netherlands	11	5.3
Germany	59	13.4	UK	17	3.0
Greece	0	0	Norway	11	0.65
Ireland	0	0	Switzerland	29	3.3
Italy	32	1.7			

Table 2. Number and total capacity of the existing incinerators in 17 European countries.

million ton of waste and 50 TWh of energy recovered (40 million ton of oil equivalents). According to Directive 2008/98/CE, a formula is indicated, Eq. (3), to clarify when the incineration of MSW is energy-efficient and may be considered a recovery operation. Indeed, the energy efficiency must be equal or above 0.6 or 0.65 depending on the installation permitted before or after 31 December 2008, respectively.

$$\text{Energy efficiency} = (E_p - (E_f + E_i)) / (0.97 \times (E_w + E_i)) \quad (3)$$

where  $E_p$  is the annual energy produced as heat (multiply by 1.1) or electricity (multiply by 2.6), GJ/year,  $E_f$  the annual energy input to the system from fuels contributing to the production of steam (GJ/year);  $E_w$  the annual energy contained in the treated waste calculated using the net calorific value of the waste (GJ/year); and  $E_i$  the annual energy imported excluding  $E_w$  and  $E_f$  (GJ/year). A corrective factor of 0.97 is introduced to accounting for energy losses due to radiation and bottom ash. It is worthwhile to refer that high efficiency is not easy to reach only through production of electricity. Hot water usage should be considered also, whenever feasible at the location.

### 3. Municipal solid waste incinerators and air pollution control technologies

Different technologies can be applied to MSW including mass burning with travelling grate, rotary kilns, modular-two stage combustion and fluidised bed (BREF, 2006). In Europe, grate incinerators are used in more than 90% of the installations and in the specific case of fluidised bed, MSW has to be pre-treated. The incineration technology used for MSW has been changing over the last 10 to 15 years, mainly driven by legislation requirements, which has forced low emission limits to air. According to Directive 2000/76/EC, a 'incineration plants' correspond to any stationary or mobile technical unit dedicated to the thermal treatment of wastes with or without recovery of the combustion heat generated. This includes the incineration by oxidation of waste as well as other thermal treatment processes such as pyrolysis or gasification in so far as the substances resulting from the treatment are subsequently incinerated. This description comprises the site and the entire incineration plant including:

- waste reception and handling (storage, on site pre-treatment facilities),
- combustion chamber (waste-fuel and air-supply systems),
- energy recovery (boiler, economizer, etc.),
- facilities for clean-up gaseous emissions,

- on-site facilities for treatment or storage of residues and waste water, stack,
- devices and systems for controlling incineration operations, recording and monitoring incineration conditions.

These areas may be distributed as indicated in Fig. 5, which represents a scheme of a typical mass burning MSW incinerator (IAWG, 1997).

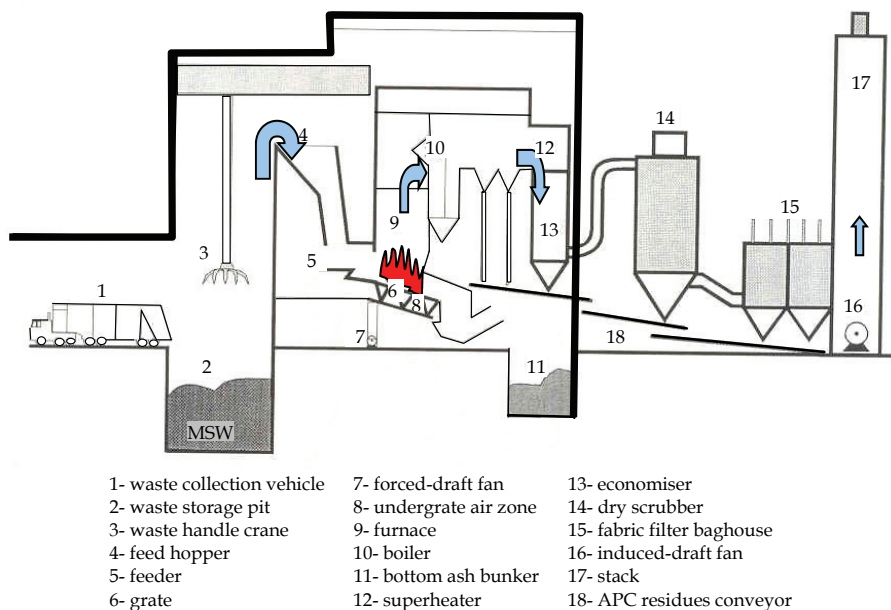


Fig. 5. Simplified scheme of a MSW incinerator (adapted from IAWG, 1997).

Considering the diagram of Fig. 5, a brief description of the mass flow into the incinerator is given below. MSW is in general delivered in trucks (1) and discharged into the storage pit "as-received" (2), in enough amounts for providing a continuous feeding material to the WtE plant. Then, waste is randomly picked up through a handle crane (3), and dropped into the feed hopper (4). The waste flows through the feeder (5) onto the moving grate (6) where combustion takes place. The plant should be controlled in order to optimize the combustion conditions, to ensure, as much as possible, complete carbon burn-out, and for this the residence time on the grate is usually no more than 60 min. The forced-draft fan (7) forces primary air through undergrate air zone (8) into the furnace (9), in order to supply oxygen to promote oxidation reactions, e.g. Eq (1). The primary air is in general taken from the storage pit (2) to lower the air pressure and eliminate most odour emissions from the storage area. Although it is not represented in Fig. 5, a secondary air supply system is common in the furnace, to guarantee turbulence of flue gases (secondary-air) and to ensure complete combustion. About 10-20% (v/v) of flue-gas is recirculated as secondary air. The reactions involved in this process are exothermic and release a high amount of energy that is carried over by the flue gases as heat. Indeed, for example, the upper calorific values of MSW in Germany are usually in the range of 7-15 MJ/kg (BREF, 2006). Energy recovery occurs mostly in boiler (10), superheater (12) and economizer (13). The burned-out bottom ashes are normally quenched and transported to a storage bunker (11). In most of the

incinerators, the bottom ashes are transported on conveyors and ferrous metals sorted, and thus at the same time metals recycling and improvement of the slag properties take place. Slag is partly vitrified and can be handled as non-hazardous or special waste in many countries. The huge amount of gases produced during combustion contains air pollutants harmful for the environment that must comply with the stringent regulatory limits. Thus, depending on the desired cleaning degree, different air pollution control (APC) systems may be used. As an example, in Fig. 5, a dry scrubber (14) and fabric filters (15) are used. In these units, APC residues are produced and further transported through a conveyor (18) for a silo (not represented). Most of the modern incinerators treat APC residues before disposed of in monofills. Finally, by using induced-draft fan (16), the cleaned flue gas is released via the stack. Concerning air pollution, it is extremely important to note that combustion includes very fast reactions (fractions of seconds) that take place in gas phase, and self-supporting combustion is possible if heat value of the waste and oxygen concentration is sufficient. Thus, grate length should ensure the phases indicated in Fig. 6.

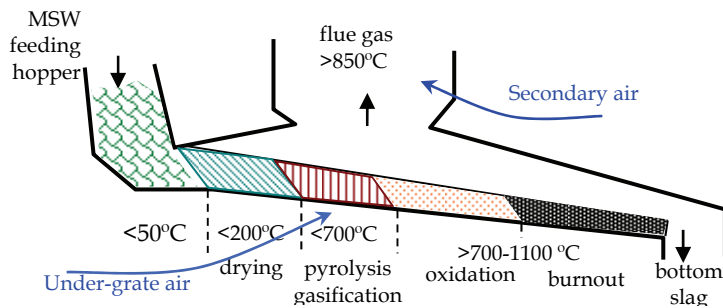


Fig. 6. Phases and temperatures on the grate of a MSWI (adapted from IAWG, 1997).

In practice, water and volatile content of MSW are evolved in the initial phase of drying at temperatures until the range of 200°C, where no oxygen is required. The next phase corresponds to pyrolysis and gasification of the organic materials, in which organic compounds are transferred to the gaseous phase. After that, in the oxidation, the combustible gases react with oxygen releasing heat and other lower weight molecules. In fully oxidative conditions, reactions are almost complete and the major gases are water, nitrogen, carbon dioxide and oxygen. It is very important to note that those phases overlap in spatial and temporal sense. Nonetheless, some in-furnace technical measures (e.g. air distribution and furnace design) can be taken to influence those stages in order to reduce pollutants in gaseous emissions (BREF, 2006). European legislation imposes a minimum gas phase combustion temperature of 850°C and at least 2 s for the residence time.

In general, MSW incineration plants operate 24 h/day and close to 365 days/year. Availability of the plant is very often over 98% and this imposes several redundancies of equipment and on-operation maintenance procedures. Fig.7 summarizes the main inputs and outputs of MSW incineration process, where it is indicated that 1 t of waste originates nearly 300 kg of bottom ashes, 30 kg of APC residues, and the rest is emitted as flue gas. The air flow rate is a control variable that is adjusted depending on the characteristics of the stack gases. However, in general about 4000 to 4500 m<sup>3</sup>/t of air is required to guarantee fully oxidizing atmosphere (IAWG, 1997). The flue gas volume originated in MSWI is dependent

on technology, in particular concerning the existence of flue gas recirculation. However, in literature there are indications that these values may be in the range of 4500 to 6000 Nm<sup>3</sup>/ton of waste (Achternbosch and Richers, 2002; BREF, 2006). Even though large local variations can be observed, typically 1 ton of MSW allows energy recovery in the range of 400-700 kWh of electricity and additional 1205 kWh as heat (BREF, 2006). In general, liquid effluents can occur from: APC devices mainly if wet systems are used, the collection and storage of bottom ash, the water/steam cycle, sanitary areas, rainwater, and cooling water. However, if re-circulation is maximized reduced amounts of wastewater are produced. Chemical reactants used in incinerator plants may be ammonium hydroxide (NH<sub>4</sub>OH) or ammonia as gas (NH<sub>3</sub>) for reducing NO<sub>x</sub> in furnace, neutralizing agents (e.g. Ca(OH)<sub>2</sub>) and adsorption materials (e.g. activated carbon). Typical consumptions rates per ton are 0.8 kg of NH<sub>4</sub>OH, 8 kg of Ca(OH)<sub>2</sub> and 0.5 kg of activated carbon.

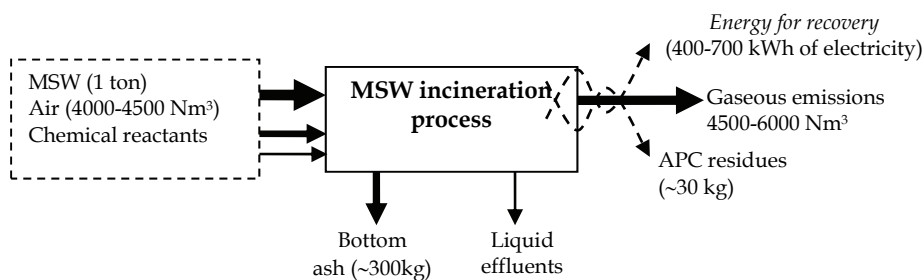


Fig. 7. Main inputs and outputs of MSW incinerators.

### 3.1 Gas cleaning systems for waste incinerators

The gas mixture leaving the incineration furnace has three main types of components that have to be removed to the possible extent before the exit at the stack:

- Fly ash which is composed by particles pneumatically transported by the gaseous flow;
- Acids and acids precursors, such as sulphur dioxide, nitrogen oxides, hydrochloric acid;
- Dioxins and analogues that are compounds formed by radical recombination with structures such as polychloro dibenzodioxins and the respective furan analogues.

The hot gas mixture leaving the furnace, exchanges heat at the surface of the heat exchanger vertical tubes, inside which the high or medium pressure steam is generated and before entering the cleaning systems, part of this gas is diverted through a booster to be injected in the cameras below the moving grate of the furnace. This gas recycling is essential in terms of overall energy recovery and also very important to promote one easier control of the stoichiometric excess of oxygen in the furnace. The remaining effluent gas mixture has to be cleaned by several unit operations in the gas cleaning systems.

### 3.2 The main targets

During the heat exchange at the surface of the boiler tubes, the effluent gas is cooled and some additional solid formation occurs, increasing the particulate fraction. This raw gas effluent of the boiler system has to be cleaned up to the environmental standards applied at the location where the incinerator is installed. The main ranges for the concentrations in the raw gas and the mandatory final emission limits most commonly used are included in



Table 3 together with the calculated efficiency required for the cleaning of each type of polluting agent. This high removal efficiency required, indicated in the Table 3, imposes the use of multiple systems for the gas cleaning, usually in sequence.

Pollutant	Concentration in raw gas from boiler (mg/Nm <sup>3</sup> )	Max admissible at exhaust (mg/Nm <sup>3</sup> )	Removal efficiency required (%)
Fly Ash	1500 - 2000	10	99,9
HCl	300 - 2000	10	> 99
SO <sub>2</sub>	200 - 1000	5	99,5
NO <sub>x</sub>	200 - 500	70	86%
HF	2 - 25	1	96%
Hg	0.2 - 0.8	0.01	99%
Cd + other metals	2 -15	0.05	>99,5
Dioxins (ng I-TEQ/Nm <sup>3</sup> )	0.5 - 5	0.1	98%

Table 3. Required efficiency for flue gas cleaning systems.

### 3.3 Unit operations for gas cleaning

A large number of unit operations based on primary separation processes can be used for the gas cleaning of the flue gas generated in waste incineration systems. In Table 4 for each type of flue gas pollutant, a combination of unit operations is indicated with the respective typical range of reduction. The well designed sequence of gas cleaning methods allows for a drastic reduction of pollutants as stated by the waste incineration BREF Table 5 (adopted with comments from Table 5.2 of the BREF, 2006).

Pollutant	Process Steps	Reduction (%)
SO <sub>x</sub>	Wet scrubber or dry multicyclone	50 - 90
HCl	Wet scrubber or semi-dry	75 - 95
NO <sub>x</sub>	Selective catalytic reduction	10 - 60
Heavy metals	Dry scrubber + electrostatic precipitator	70 - 95
Fly ash *	Electrostatic precipitator + fabric hose filter	95 - 99,9
Dioxins & Furans	Activated carbon + fabric hose filter	50 - 99,9

\*Very often the fly ash surface has adsorbed other pollutants such as dioxins and heavy metals

Table 4. Gas cleaning processes and typical range of specific pollutant reduction by combination of unit operations.

### 3.4 Separation of fly ash and activated carbon

Fly ash generated at power plants where the composition of the fuel is reasonably constant, is very often collected and used as raw material for the production of Portland cement. Fly ash generated at waste incinerators is usually contaminated with heavy metals and other dangerous substances and have to be treated as a hazardous residue, requiring inertization before the disposal is controlled landfill.

Substance	Non-Continuous samples	Half-hour mean value	Daily mean value	Notes
Dust		1-20	1-5	Lower levels achieved with fabric filters as hose bags filters
HCl		1-50	1-8	Use of wet processes preferred
SO <sub>2</sub>		1-150	1-40	Use of wet processes preferred
NO <sub>x</sub> with SCR		40-300	40-100	Additional energy demand and costs
NO <sub>x</sub> with SCR		30-250	120-180	At high raw gas NO <sub>x</sub> levels, NH <sub>3</sub> slip to be taken into account, preferred method in conjunction with wet processes
TOC		1-20	1-10	Optimum combustion conditions are required
CO		5-100	5-30	Optimum combustion conditions
Hg	<0.05	0.001-0.03	0.001-0.02	Input control, carbon-based adsorption processes
PCDD/PCDF (ng ITEQ/Nm <sup>3</sup> )	0.01-0.1			Optimum combustion conditions, temperatures controls to reduce synthesis, carbon-based adsorption processes.

Table 5. Attainable emission levels for waste incineration facilities (excerpt from Table 5.2 of BREF (2006) "Operational emission levels associated with the use of BAT" for air pollutants expressed in mg/Nm<sup>3</sup>).

The activated carbon, in powder form, is very often used to adsorb organic pollutants such as dioxins and furans, as it will be detailed later on, this powder is collected together with the fly ash (small systems) in a specific stage of cleaning. The main type of equipments used for the removal of solid particles of the fly ash and activated carbon are: cyclones, electrostatic precipitators, and fabric hose filters, Table 6. Construction details, as well as operating modes have been described extensively (Niessen, 2002) and therefore it was considered more relevant to focus the detail here on the range of applicability for the fly ash separation.

### 3.4.1 Cyclones

Cyclones are rather efficient for the removal of solid particles with average diameter over 100 µm from gaseous flows. The design of cyclones was reviewed elsewhere (Morcos, 1989; Lee and Huffman, 1996; Amutha Rani et al., 2008) and since for their construction steel or stainless steel can be used the range of permissible operating temperatures is rather wide. In gas cleaning of flue gas from incinerators cyclones are very often used as primary separators followed by other separating units designed for the retention of particles of the lower size present in the fly ash.

### 3.4.2 Electrostatic precipitators (ESP)

Nearly one century ago, Dr. Frederick Cottrell introduced the concept of particle separation by the application of an electric field. Overall efficiency of ESP depends mainly on the plates and rapper design, and collection zones have to be carefully designed to assure the adequate thickness of laminar boundary layer, in order to prevent reentrainment into the gas stream the aggregate formed with the collected particles. Typical gas velocities inside the precipitation zone are always below 1 m/s and very often below 0.5 m/s. Electrostatic

precipitation, as many other process equipment items in an incineration plant have to be adjusted to steady state conditions but with the control system prepared to modulate under unbalance to peak conditions. Dynamic control is often required and the fine control of efficiency is of utmost importance (Bordado and Gomes, 1999).

Equipment	Typical efficiency for fly ash	Typical efficiency for AC	Typical pressure drop range	Maximum operating temperature	Range of particles sizes
Cyclones	up to 80%	up to 50%	10 to 1000 Pa	1300 °C	≥ 20 μm
ESP	up to 99%	up to 80%	50 to 300 Pa	450 °C	0.08 to 20 μm
Fabric hose filters	up to 99%	up to 99%	500 to 2000 Pa usually with a booster fan	240 °C	0.04 to 50 μm

Table 6. Fly ash and activated carbon (AC) separation.

### 3.5 Separation of acids

The acids present in the flue gas, such as HCl and HF and the precursor of acid SO<sub>2</sub> can be separated by different processes: dry process (with the use of a solid adsorbent); semi dry (with the use of a spray absorber); wet process (with aqueous solutions).

Criteria	Wet FGT (W)	Semi-Wet FGT (SW)	Dry line FGT (DL)	Dry Sodium bicarbonate FGT (DS)
Air emissions performance	+	0	-	0
Residue production	+	0	-	0
Water consumption	-	0	+	+
Effluent production	-	+	+	+
Reagent consumption	+	0	-	0
Ability to cope with inlet variations of pollutant	+	0	-	0
Plume visibility	-	0	+	+
Process complexity	-	0	+	+
Costs - capital	generally higher	medium	generally lower	generally lower
Costs operational	medium	generally lower	medium	generally lower

#### Note

+: means that the use of the technique generally offers an advantage in respect of the assessment criteria considered

0: the technique offers no significant advantage or disadvantage in respect of the assessment criteria considered

-: means that the use of the technique generally offers a disadvantage in respect of the assessment criteria considered

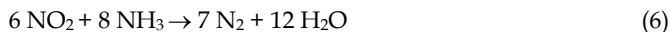
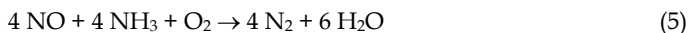
Table 7. An example assessment of some IPPC relevant criteria that may be taken into account when selecting between wet/semi-wet/dry flue gas treatment (FGT) options.

As solid adsorbents, the dry lime (calcium hydroxide) is more commonly used but dry sodium bicarbonate can also be an option. A comparison of the specific processes for acids separation is qualitatively presented in Table 7. Each one of these alternatives has nowadays several variants and refinements but it was considered out of the scope of this review the fine detail of the multiple available alternatives.

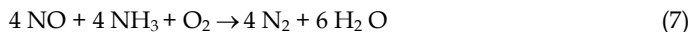
### 3.6 Nitrogen oxides reduction

Nitrogen oxides content in flue gas are usually reduced by two reactive processes: SNCR (selective non-catalytic reduction) and SCR (selective catalytic reduction). Other chemical process focused on the reduction of  $\text{NO}_x$  formation during the combustion have been extensively studied at laboratory and pilot plant level, and may be based on radical quenchers that minimize  $\text{N}_2$  oxidation by radical reactions. However most, if not all those processes, have a large negative impact on combustion efficiency and consequently they cause an increase content of VOC and namely PAH in the flue gas.

The SNCR process uses ammonia ( $\text{NH}_3$ ) as reactant or for smaller systems urea ( $\text{CO}(\text{NH}_2)_2$ ) as reducing agents, with direct injection into the furnace. At high temperature, urea decomposes with ammonia formation, Eq.(4), and the main overall reduction reactions take place between 850 °C and 1050 °C according with the schemes Eq.(5)-(6):



The SCR process (Jungtten et al., 1988) uses a solid catalyst usually in a fixed bed and operates between 200 as 400 °C, in presence of ammonia. This range of operating temperature and the fact that catalysts deactivate in presence of strong acid media, imposes the SCR module to be installed after particulate material, as well as acidic components are already removed from flue gas. The more representative overall reactions taking place at the surface of the catalyst are indicated by Eq. (7)-(9). A comparison of the main features SNCR and SCR processes is presented in Table 8.



### 3.7 Carbon monoxide and volatile organic compounds

The increase of carbon monoxide (CO) and/or volatile organic compounds (VOC) content in the flue gas is a strong indication of inappropriate burning conditions in the furnace. Several adjustments by the control systems can be adopted, but the more common are:

- i. Increase of raw air inlet to the furnace;
- ii. Reduction of flue gas recycling to the furnace;
- iii. Slight increase of pressure below the grid.

Both i) and ii) will increase the stoichiometric excess of air in the furnace, allowing for a more complete oxidation of the wastes, and of the respective volatiles, such as thermal

	SNCR	SCR
Advantage	Lower investment cost Lower corrosion problems	More efficient
Disadvantage	Limited efficiency	Higher investment cost Higher pressure drop Requires higher O <sub>2</sub> excess
Efficiency for NO <sub>x</sub> reduction	Up to 70% Typical 30 to 60%	Up to 85% Typical 50 to 80%

Table 8. SNCR versus SCR processes for NO<sub>x</sub> reduction.

degradation products. For wastes with a rather high content of halogens or phosphorus (for example in presence of increased content of flame retardants and/or PVC), the adoption of i) and specially ii) will be very effective, but increase of stoichiometric oxygen over 10% usually results in an overall energy recovery efficiency reduction due to energy consumption to heat-up the unavoidable N<sub>2</sub> inlet. The adoption of iii) is especially effective for wastes with high moisture content, resulting in a more effective lifting of the waste material from the moving grate. It is important to refer that measure iii) can only be adopted with the so called high pressure drop grates in which the grate perforations and gaps are rather small (for example VON ROLL type grates).

Separation of carbon monoxide and volatile organic compounds present in the flue gas is not an easy task. One of the very few specific processes, worth to refer, is the catalytic oxidation in heterogeneous converter. In general terms, additional O<sub>2</sub> is injected in the flue gas stream and this mixture is further oxidized over a fixed bed of a strong oxidation catalyst such as platinum non woven felts.

For rather small waste incinerators, and when the waste has one high content of PVC disposables (e.g. hospital waste) this oxidation step is included in the gas cleaning system, usually close to the boiler since the oxidation is more effective at high flue gas temperatures. For larger systems such as ones used for mass burning of municipal wastes this systems is very seldom included in the design due to the very high specific investment cost and also due to the additional loss of energy due to boosting requirements to compensate the pressure drop.

### 3.8 Moisture condensation in gas cleaning systems

Moisture condensation is one of the major problems that can occur in gas cleaning systems. The occurrence of condensation causes drastic corrosion problems as well as fly ash aggregation as a mud or "paste" and induces the malfunction of several gas cleaning steps mainly the hose fabric filters. Both in the design as well as in the operation of incineration systems, to avoid moisture condensation is mandatory and in case of continuous occurrence the life span of the overall plant will be reduced as well as the average availability due to more frequent cleaning and maintenance requirements.

Incidence on operating costs is therefore also significant, and although several mitigating measures can be adopted from the control point of view, the best may be of course to prevent its occurrence by a careful design of the plant. Not only the overall water balance has to be considered for steady and dynamic conditions but careful estimation of the dew point of the flue gas in different critical points must be performed.

The main contributions for the total water present in the flue gas come from:

- i. Moisture in the inlet air;

- ii. Moisture vaporized from the wastes;
  - iii. Water formed in the combustion reactions;
  - iv. Water vaporized in the flue gas stream in the wet or semi-wet cleaning steps;
- Rather high values of i) and ii) are expected to occur simultaneously in rainy days or if snow accumulates on the waste at the collection points, and therefore active prevention of condensation is of utmost importance at the design stage.

The flue gas temperature, from the outlet of the boiler until the stack, is becoming lower, partly due to energy recovering systems, and therefore the probability of the occurrence of condensation becomes higher toward the last stages of the gas cleaning system.

Re-heating of the flue gas, to avoid condensation can be achieved in practice by different processes. The more common ones are:

- i. Injection of limited flow of hot flue gas boosted stream in the main stream: this is very effective system of re-heating, but it has the disadvantage that hot flue gas from the boiler is more contaminated, and the overall cleaning efficiency is slightly reduced;
- ii. By heat exchanging with hot flue gas: in this case the two streams are kept separated and the only drawback is the increased pressure drop through the heat exchanger and the higher investment cost.

In both cases the heat-up to, say 2 to 5 degree centigrade over the higher dew point temperature that can occur is usually effective to prevent condensation since the pressure profile is, as a rule, very stable. To prevent condensation, the re-heating is very often considered in the design at least in two points of the cleaning system:

- i. Immediately before the exhaust stack to avoid the formation of "plume" caused by condensation during cooling by the cold air;
- ii. Before the hose fabric filters to avoid clogging by mud formation in the inside wall of the filter.

The use of corrosion resistant materials and special coatings where condensation is more prone to occur, is indeed a good design practice, but to prevent the occurrence is certainly also of major importance.

### **3.9 Emerging technologies for gas cleaning**

#### **3.9.1 Oil and emulsion scrubbing**

Dioxins and polyaromatic hydrocarbons (PAH) have a very limited solubility in aqueous solutions and therefore their removal by aqueous wet scrubbers is rather limited. A small depletion is observed due to condensation in the rather cold water solution, as well as in the sludge of solid particles at which surface they remain adsorbed, but due to their marked lipophilic character they tend to float and eventually be removed from the scrubbing solution by the gas flow.

High boiling oils, partly unsaturated proved to be an efficient scrubbing media, as well as their respective oil-in-water emulsions stabilized by non-ionic surfactants with HLB between 7 and 10 (Encyclopedia of emulsion technology, 1988). The oil emulsion retains mostly dioxins, furans and PAH and it is considered a good practice to dispose the emulsion as soon as total content of those pollutants reaches 0.1 mg/L. The design of the scrubbing systems considers a buffer volume of emulsion that allows for the emulsion exchange up to 4 times per year in the worst operating conditions. Emulsion preparation vessel and transfer pump is therefore to be included in the auxiliary equipment.

Disposal of the contaminated emulsion includes an emulsion breaker, liquid-liquid separation and absorption of the oil phase in wood particles or other lipophilic absorber, such as open cell polyurethane (Clark et al., 2008) or phenolic foam, and the feeding of the solid material for the furnace for further energy recovery.

A separate burner for the oil into the furnace can also be installed, but operators of waste incinerators do not like to feed liquids or oils to the furnace for a large number of operational problems that can occur.

### 3.9.2 Dedusting and particle aggregation

Although very efficient for over 99% of the particles the electrostatic precipitators and the fabric hose filters are not effective for nanoparticles as well as for the smaller sub-micron particles. Flue gas exhaust at the stack, although very clean has however a small content of nanoparticles. Recent concerns on the physiological effect of respirable nanoparticles induced research on their study and on methods of avoiding their presence in the exhaust flue gas. Improving particle aggregation and dedusting seems the more promising alternative and intense research is being conducted in that direction. So far it was proved that very fine dust and nanoparticles can be effectively aggregated by water dispersible polymers with controlled water compatibility (Nunes et al., 2011).

## 4. Main pollutants released during MSWI and the European legislation

The main direct impacts caused by incineration are emissions to air, residues production (bottom ash and APC residues), emissions to water, energy production/consumption, material consumption, noise and vibration, fugitive emissions (including odour mainly from waste storage), storage/handling/processing risks of wastes. Among these, emissions to air are really significant, since the incineration of 1 ton of MSW produces a huge volume of flue-gas. Some measurements revealed that 4500-6000 Nm<sup>3</sup>/ton (at 11% O<sub>2</sub>) are usually emitted. Depending on the technology, operating conditions and the composition of waste incinerated, diverse pollutants are formed and emitted in flue gas:

- particulate matter – with a broad distribution size;
- acids and other gases– HCl, HF, HBr, HI, SO<sub>2</sub>, NO<sub>x</sub>, NH<sub>3</sub>, ...;
- heavy metals – Hg, Cd, Tl, As, Ni, Pb, Sb, Se, Sn, Zn, ...;
- carbon compounds – CO, VOC, PCDD/PCDF, PCB, PAH,...;

In this scope, measures for reducing pollutant precursors in wastes, such as chlorine and volatile heavy metals, may have positive effects. In practical terms, redesign products and packages could be an important aspect for reducing emissions. With respect to heavy metals, it is important to avoid batteries, leather, pigments, cans, and for reducing chlorine, wastes such as plastics (PVC) must be avoided.

Since the early 1970s Europe has been strongly committed to the environment protection of air. In this ambit, it should be mentioned the Directive 2000/76/EC of the European Parliament and of the Council, on the incineration of waste that aims “to prevent or to limit as far as practicable negative effects on the environment, in particular pollution by emissions into air, soil, surface water and groundwater, and the resulting risks to human health, from the incineration and co-incineration of waste.” This Directive, known as Waste Incineration Directive (WID), states that continuous measurements of NO<sub>x</sub>, CO, total dust, TOC, HCl, HF and SO<sub>2</sub> should be carried out, and at least twice a year for heavy metals (Cd, Tl, Hg, Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V) and dioxins and furans. In fact, WID imposes very restrictive limit values for the

main air emission pollutants. For example, the emission limit value allowed to the total concentration of dioxins and furans calculated using the concept of toxic equivalence is 0.1 ng I-TEQ/Nm<sup>3</sup>. Table 9 shows the air legal limits values indicated in WID, as well as the usual ranges that can be observed before treatment of flue-gas (crude flue-gas).

	Before treatment (BREF, 2006)		After treatment (BREF, 2006)	Legal limits*
Dust (mg/Nm <sup>3</sup> )	1000-5000	2000-10000	0.1-4	10
CO (mg/Nm <sup>3</sup> )	5-50		2-45	50
TOC (mg/Nm <sup>3</sup> )	1-10		0.1-5	10
HCl (mg/Nm <sup>3</sup> )	500-2000	400-1500	0.1-6	10
HF (mg/Nm <sup>3</sup> )	5-20	2-20	0.01-0.1	1
SO <sub>2</sub> (mg/Nm <sup>3</sup> )	200-1000	200-800	0.2-20	50
NO+NO <sub>2</sub> (mg/Nm <sup>3</sup> )	250-500	200-400	20-180	200 #
NO (mg/Nm <sup>3</sup> )	<40			not defined
Hg (mg/Nm <sup>3</sup> )	0.05-0.5	0.3-0.8	0.0002-0.05	0.05
Cd,Tl (mg/Nm <sup>3</sup> )	<3	3-12	0.0002-0.03	0.05
Other heavy metals (Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V)	<50		0.0002-0.05	0.5
Dioxins and Furans (ng I-TEQ/Nm <sup>3</sup> )	0.05-10	<1-5	0.0002-0.08	0.1
CO <sub>2</sub>	5-10%			not defined
H <sub>2</sub> O	10-20%			not defined

Ref.1 – Achternbosch and Richers (2002), \*set on Directive 2000/76/EC, #for nominal capacity ≥ 6 ton/h or new incineration plants.

Table 9. Concentrations of gaseous emissions before and after treatment and legal limits.

To prove compliance with the emission values set in WID, measured concentrations,  $C_M$ , shall be standardised (indexed with S),  $C_S$ , at the following conditions: 273 K, 101.3 kPa, 11 % O<sub>2</sub>, and dry gas ( $M_S=0$ ) by using the following equation:

$$C_S = C_M \frac{21 - O_{2,S}}{21 - O_{2,M}} \frac{100 - M_S}{100 - M_M} \frac{T_M}{T_S} \frac{P_S}{P_M} \quad (10)$$

where oxygen concentration ( $O_{S,M}$ ), moisture ( $M_M$ ), temperature ( $T_M$ ) and pressure ( $P_M$ ) represent the measured conditions.

The emissions of pollutants such as HCl, HF, SO<sub>2</sub>, NO<sub>x</sub> and heavy metals depend mostly on the waste characteristics and air pollution control devices. Furnace technology determine to a great extent CO, VOC and NO<sub>x</sub>. The total dust emitted is determined upon APC devices. Fig. 8 shows a mass balance in respect to some pollutants per 1 ton of MSW incinerated.

#### 4.1 Dust

During the incineration process, part of the waste is incombustible and removed from the incinerator as solid wastes, usually referred as bottom ash or slag, APC residues and very low quantity of residual particles in the flue gas. The matrix compounds of these particles are mainly aluminium and silicon oxides. Concerning air pollution from MSWI, the most import fraction is the finest inorganic particles that remain after the combustion of the



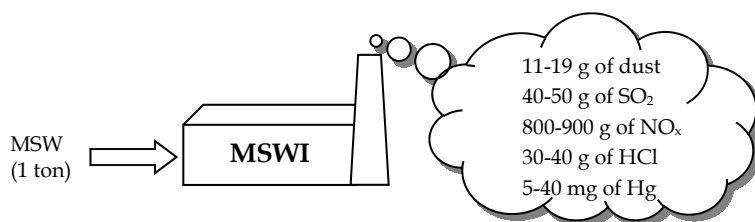


Fig. 8. Mass balance in respect to some pollutants in stack gases.

waste and pass with the flue gas out of the furnace. Some of these particles settle as boiler ash and are removed in the hoppers. A very important aspect concerning air pollution is the fact that as flue gas cools diverse gaseous compounds (some pollutants) condense on the particle surfaces. Since high concentration of HCl is present in the boiler, the condensate phases may include diverse metals chlorides such as ZnCl<sub>2</sub>, PbCl<sub>2</sub> and CdCl<sub>2</sub> (World Bank Report, 1999).

Particulate matter is often grouped into categories based on their diameters (e.g. PM<sub>2.5</sub> with a diameter less than 2.5 µm). For example, PM<sub>2.5</sub> may persist in the atmosphere for long periods, travelling long distances and they are capable to penetrate deep into the respiratory tract. Their toxicity is normally correlated with the respective chemical composition.

Air pollution control (APC) residues produced in incineration plants are classified as hazardous solid waste mainly due to its high alkaline pH, high content in volatile heavy metals and soluble salts, and trace amounts of very toxic compounds such as dioxins and furans (Quina et al 2008b). The current APC disposal methods in use are very limited, and in the near future they are likely to become unsustainable, due to stringent environmental regulations. Development of new and safer inertization processes will be a must in the future. When APC residues are formed in devices with Ca(OH)<sub>2</sub> injection, reaction products such as CaOHCl, CaF<sub>2</sub>, CaSO<sub>3</sub> or CaSO<sub>4</sub> may be present in considerable concentration, as result of HCl, HF and SO<sub>2</sub> gases neutralization. Often activated carbon is also added which also ends up in APC residues.

#### 4.2 Carbon monoxide

Carbon monoxide (CO) is a gas that can be found in the flue-gas as a product of the incomplete combustion of organic compounds that is measured on-line and usually used to check the incineration efficiency. In MSWI it is usual to assume that when CO concentration is low in flue-gas then the gas burn out has high quality, and the TOC emissions are low in those conditions. CO arises in combustion chambers when there is not enough O<sub>2</sub> for full oxidation or if temperature is not high enough to guarantee full reaction to CO<sub>2</sub>. Carbon monoxide oxidation to carbon dioxide occurs after some time of its release to the atmosphere (BREF, 2006).

#### 4.3 Volatile organic compounds

Volatile organic compounds (VOC) are products of incomplete combustion and may cover a wide range of compounds, since they can include carbon chains or rings that have high vapour pressure (e.g. 0.27 kPa at 250 °C). When combustion operates at high efficiency, very

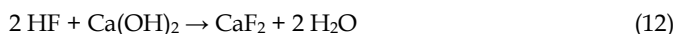
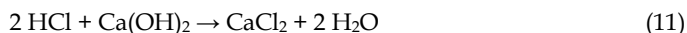
low concentrations of organic compounds are expected into air emissions. Indeed, in general, flue-gas from MSWI only contains trace quantities of volatile organic compounds (VOC) that are quantified on-line in the flue-gas as total organic carbon (TOC). Commonly speciation of VOC may include compounds such as methane, ethane, propane, butane, pentane, hexane, heptane, ethylene, benzene, toluene and xylene (BTX), ethylbenzene, acetylene, formaldehyde, acetone, etc. Methane ( $\text{CH}_4$ ) is not formed as long as oxidative conditions are observed in WtE process. In fact,  $\text{CH}_4$  may only arise in the waste bunker, due to anaerobic processes during long periods of storage.

Beyond the organic compounds referred above, traces of polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and dioxins (PCDD/PCDF - discussed in section 4.10) may occur in flue-gas, mostly adsorbed into particles.

#### 4.4 Acid chloride and fluoride

Chlorine and fluorine may be present in MSW in significant quantities. The main sources of chlorine are plastics such as PVC, salty food waste and other inorganic chlorides. Fluorine can arise into plastics such as PTFE, fluorinated textiles and other inorganic fluorides. Under the furnace conditions chlorine and fluorine are mostly converted into acid hydrogen halides, HCl and HF, and part of these may react to form metal chlorides.

In general, HCl and HF are removed by the same technology, by adding neutralization agents, for instance lime ( $\text{Ca}(\text{OH})_2$ ), sodium hydroxide (NaOH), or calcium carbonate ( $\text{CaCO}_3$ ). The following reactions show the separation of acid pollutants with  $\text{Ca}(\text{OH})_2$



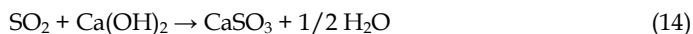
These reactions may entail complex mechanisms due to various gas/solid phases involved, and some studies refer that instead  $\text{CaCl}_2$  the main phase formed is  $\text{CaOH}$  (Quina et. al. 2008b). Gaseous emissions concentrations are in general in the range of 0.1 -6  $\text{mg}/\text{Nm}^3$  for HCl and 0.01 -0.1  $\text{mg}/\text{Nm}^3$  for HF, and thus below the regulatory limits.

#### 4.5 Sulphur dioxide

Sulphur dioxide is a reaction product of S-compounds contained in the waste with oxygen, and its concentration in the flue-gas is proportional to the amount present in the waste:



Regardless of whether in organic or inorganic forms, most of the sulphur oxides end up in stack gases as  $\text{SO}_2$ . According to BREF (2006), in spite of the regulatory threshold of 50  $\text{mg}/\text{Nm}^3$ , most of the installations reveal emissions lower than 20  $\text{mg}/\text{Nm}^3$ . This pollutant can be removed by the reactions:



It is important to note that  $\text{SO}_2$  is a highly reactive gas with short half life indoors. Although it is a known respiratory irritant and bronchoconstrictor, its effects seem limited to patients with asthma and bronchitis, while sensitivity to exposure varies widely (Katsouyanni et al., 1997). In some cases,  $\text{SO}_2$  is highly correlated with fine particles, and thus these pollutants

may be surrogates for each other. Sulphur dioxide is also known as highly toxic for Koch's bacillus and thus, the incidence of tuberculosis is recognized as lower in areas of  $\text{SO}_2$  release.

#### 4.6 Nitrous dioxides

Nitrogen oxides,  $\text{NO}_x$ , are well known acidic and global warming gases, and during incineration process three main different mechanisms can lead to their formation. Indeed, part of the air nitrogen and part of the nitrogen contained in the waste (or fuel) may be oxidized to  $\text{NO}_x$ . The nitrous oxides produced from air are known as *thermal*  $\text{NO}_x$ , and the ones originated from waste as *fuel*  $\text{NO}_x$ . These reactions can significantly occur for temperatures above 1300 °C and whenever oxygen is not a limiting reagent. In WtE plants, thermal  $\text{NO}_x$  is often much greater than fuel  $\text{NO}_x$ . The formation of nitrogen oxides through radical reactions with organic compounds is known as *prompt*  $\text{NO}_x$ , and has little contribution in WtE incineration plants.

Legislation set a regulatory limit of 200 mg/Nm<sup>3</sup>, and to comply with this limit, primary and secondary measures may be taken. The main primary techniques can involve both over supply air and excessive high furnace temperatures. Secondary measures may demand injection of reduction agents such as ammonia (as 25% aqueous solution) or urea, for promoting SNCR indicated in Eq. (5)-(6) (section 3.6).

The reduction of  $\text{NO}_x$  can attain 85% at temperature of 1000°C, and thus some  $\text{NH}_3$  can also be released in the flue-gas (BREF, 2006). When urea is used as reducing agent in SNCR, a little  $\text{N}_2\text{O}$  may arise. Nitrous oxide ( $\text{N}_2\text{O}$ ) is usually correlated with CO, since it is formed under low oxygen concentrations, but it is not included in  $\text{NO}_x$  emissions. Alternatively, SCR by using specific catalysts can be integrated in the APC area, after acid neutralization and dedusting. Depending on the catalyst, SCR reactions can take place in the range of 180 to 450°C. Stack emissions typically exhibit 95% of NO and 5% of  $\text{NO}_2$  (BREF, 2006). Specific emission of  $\text{NO}_x$  may be in the range of 800-900 g/ton of MSW.

#### 4.7 Mercury

Mercury is by far the most thermally mobile metal, highly toxic, and at 357 °C it is all volatilized into the flue gas. Although restriction in uses of Hg, some peak loads of MSW with batteries, electrical devices, thermometers and specific wastes may lead to incompliance with the regulatory threshold of 0.05 mg/Nm<sup>3</sup>.

The oxidation state of Hg depends mostly on the characteristics of the flue-gas, but in general, the most significant forms in MSWI are  $\text{Hg}^0$  and  $\text{HgCl}_2$ . When the HCl concentration in flue-gas is higher than  $\text{SO}_2$  (a reduction agent), mercury is mainly in the form  $\text{HgCl}_2$ , which is easier to remove from the gas phase than  $\text{Hg}^0$ .

For this element, the primary measures are those which avoid as much as possible to introduce in the furnace contaminated wastes that contain Hg. Nevertheless, secondary techniques are usually implemented in order to comply with the regulatory limit at stack emissions. The lowest emissions of Hg are observed when sulphur doped activated carbon is used. Some analysis showed that wet acidic scrubbers can serve as a sink for Hg if it occurs in chloride form (BREF, 2006). The amount of Hg in MSW is in the range of 0.5- 5 g Hg/ton MSW, and from this less than 2% goes to bottom ashes, 70-90% is released into APC residues, and less than 10% is emitted to air emissions, which correspond to 0.0002-0.05 mg/Nm<sup>3</sup> (IAWG, 1997).

#### 4.8 Cadmium and thallium

Cadmium is an environmental problematic toxic element that may arise in air emissions of MSWI due to its thermal mobility. Although some countries restrict applications of Cd, frequent sources in MSWI are electronic devices (including accumulators), paints, Ni-Cd batteries, and cadmium-stabilised plastics. Under the conditions usually observed in the furnace, Cd is mainly converted into  $\text{CdCl}_2$ . The APC devices normally lead to a concentration of Cd in APC residues, and less than 1% is released to the atmosphere. The reported range is usually 0.0002-0.03 mg/Nm<sup>3</sup> (11% of O<sub>2</sub>) (BREF, 2006).

The thallium amount in municipal solid waste is virtually non-existent and very often below any detection limit.

#### 4.9 Other heavy metals

During the main stages of incineration, combustion temperatures attained in the furnace determine the evaporation degree of heavy metals and most of inorganic salts. Indeed, besides Hg, Cd and Tl also Sb, As, Pb, Cr, Co, Cu, Mn, Ni and V must be under control in stack emissions. These are very toxic metals since they are carcinogenic or may provoke respiratory damages. Most of these metals are in flue-gas as oxides or chlorides, which condense onto dust particles as the gases cool down downstream of the boiler. Therefore, it is expected that the part of these metals that vaporize in furnace, probably ends as condensed phases in APC residues. Thus, according to measurements in diverse European incinerators, the limit of 0.5 mg/Nm<sup>3</sup> is usually complied (BREF, 2006). Lead and chromium are currently the most problematic heavy metals found in APC residues that lead to a classification as hazardous waste (Quina et al, 2008b).

#### 4.10 Dioxins

Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are commonly referred as *dioxins* and include a set of tricyclic aromatic persistent organic pollutants (POPs), that are ubiquitous in the environment and may provoke significant risk to human health (WHO, 1989). Recently, Hites (2011) presented a short but very interesting overview and history about dioxins, where it is referred that PCDD/PCDF is now a well-known environmental contaminant family. In fact, depending on the position of chlorine in the benzene ring, 210 congeners can be formed. Fig. 9 (a)-(b) shows the generic structure of dioxins and furans, where chlorine may be attached at positions  $m=1-4$  and  $n=6-9$ , and thus, it is possible to form 75 dioxin and 135 furan congeners. The most toxic dioxin is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) and it has been considered as molecule characterized with the lowest lethal dose to 50% of a population (LD<sub>50</sub>). For example, for guinea pigs, LD<sub>50</sub> is only 0.6 µg/kg. PCDD/PCDF are in general very lipophilic, solid at room temperature, with low volatility and insoluble in water. Thus, their dispersion in atmosphere is likely to occur mainly in particulate matter.

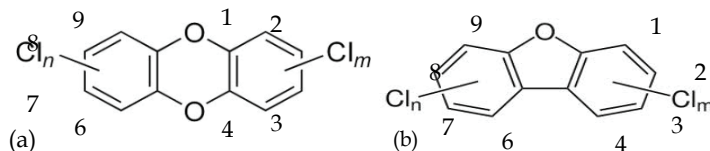


Fig. 9. Generic structure of (a)- polychlorinated dibenzo-*p*-dioxin (PCDD), (b)- polychlorinated dibenzofurans (PCDF).

PCDD/PCDF are considered unintentionally produced persistent organic pollutants (POPs), in respect to which the Stockholm Convention obliges Parties to decrease the total release. According to UNEP Chemical (2005) these by-products are formed in various processes and activities (e.g. waste incineration, metal and mineral production, heat and power generation, transport, open burning, production and use of goods) or they can be introduced into processes as contaminants in raw materials (e.g. disposal of wastes). In 1977, Olie and co-workers showed that PCDD/PCDF are in trace quantities in fly ashes and flue gases of MSW incinerators (Olie et al., 1977). Since then, it is well known that dioxins are formed in trace quantities in incineration processes (UNEP Chemical, 2005). McKay (2002) reviewed methods to minimise the formation of these very toxic compounds in MSWI. Indeed, in addition to PCDD/PCDF originally present in the furnace feedstock, three formation theories should be considered:

- precursor compounds such as chlorinated hydrocarbons already in the MSW feed or formed in furnace by reacting rapidly with other groups (e.g. chlorobenzene);
- *de-novo* synthesis of smaller and relatively innocuous chemical molecules combining together in the low temperature range;
- radical recombination with prevalence of the structures with longer life-span (more symmetrical and more stable).

The maximum formation rate of dioxins is in the range 300–400 °C, and the knowledge of this fact associated with the information about the reaction mechanisms have been the basis of designing combustion systems (McKay, 2002). Therefore, two strategies have been adopted for complete destruction in combustion and for minimize their formation. In this scope, it is very important that the combustion temperature should be above 1000 °C, the residence time should exceed 2 s, and high turbulence in the combustion chamber should be promoted (Reynolds number higher than 50,000). As an end-of-pipe treatment, it should be assured that a very rapid gas cooling from 450 to 250 °C is able to occur. Currently, semi-dry lime scrubbing and bag filters coupled with activated carbon injection have been playing an important role in prevention or minimisation of dioxins in stack gas emission to the environment (McKay, 2002). In addition, after the regulatory limit of 0.1 ng I-TEQ/Nm<sup>3</sup> entered into force, MSWI is no longer a significant sources of dioxins. In fact, some nineties studies refer that MSWI seem to be the most important source of PCDD/PCDF to air emissions (Olie et al., 1998). However, the emissions of MSWI of units that comply with the limit established in Directive 2000/76/EC are no longer so important (Abad et al., 2003; Lee et al., 2007). Indeed, measurements for MSWI plants, equipped with up-to-date APC systems showed that average concentration is around 0.048 ng I-TEQ/Nm<sup>3</sup>, and the monitored values are all in the range 0.01–0.08 ng I-TEQ/Nm<sup>3</sup> (Abad et al., 2006). Table 10 shows the concentration of the seventy congeners that should be taken into account to calculate the equivalent toxicity (I-TEQ), from four different references (Ref1–Ref4).

At this point it is important to note that there is evidence that some additional treatment systems for flue gas may result in a dramatic decrease in dioxins concentrations emitted in stack flue gas, having been reported reductions of 99.98% (Lee et al., 2007). On the other hand, while the concentrations are very low, these chemicals are highly toxic. In 1997, the International Agency for Research on Cancer declared the 2,3,7,8-TCDD to be carcinogenic to humans (Abad et al., 2006). PCDD/PCDF are among the most widely studied organic chemical and there are a large number of publications on the toxicological effects (WHO 1989; Van Den Berg et al., 1994; Mukerjee, 1998). The effect of dioxin on humans is associated with increased risk of chloracne and hyperpigmentation, changed liver function

Congener	Ref1 (pg/Nm <sup>3</sup> )*	Ref2 (ng/Nm <sup>3</sup> )	Ref3 (ng/Nm <sup>3</sup> )	Ref4 (ng/Nm <sup>3</sup> ) 1996 2000	
2,3,7,8-TeCDD	0.34 ± 0.23	0.00259	0.0003	1.29	0.007
1,2,3,7,8-PeCDD	3.53 ± 2.23	0.00886	0.0004	15.41	0.026
1,2,3,4,7,8-HxCDD	5.92 ± 3.13	0.0109	0.0010	21.10	0.032
1,2,3,6,7,8-HxCDD	27.0 ± 16.6	0.0299	0.0010	48.88	0.085
1,2,3,7,8,9-HxCDD	11.2 ± 6.83	0.0155	0.0000	55.28	0.074
1,2,3,4,6,7,8- HpCDD	204.7 ± 104.4	0.213	0.0000	227.66	0.533
OCDD	403.6 ± 198.4	0.340	0.0000	251.24	0.665
2,3,7,8-TeCDF	9.25 ± 14.2	0.0190	0.0000	94.10	0.029
1,2,3,7,8-PeCDF	12.6 ± 8.1	0.0222	0.0000	10.81	0.010
2,3,4,7,8-PeCDF	30.0 ± 15.3	0.0388	0.0010	81.04	0.028
1,2,3,4,7,8-HxCDF	25.4 ± 13.1	0.0306	0.0000	121.76	0.052
1,2,3,6,7,8-HxCDF	46.3 ± 24.1	0.0350	0.0010	69.21	0.050
2,3,4,6,7,8-HxCDF	86.4 ± 46.9	0.0516	0.0010	10.47	0.003
1,2,3,7,8,9-HxCDF	21.4 ± 13.9	0.00446	0.0010	135.83	0.102
1,2,3,4,6,7,8- HpCDF	145.0 ± 93.5	0.110	0.0000	227.06	0.231
1,2,3,4,7,8,9- HpCDF	52.7 ± 34.9	0.0240	0.0000	68.01	0.040
OCDF	219.1 ± 210.0	0.0906	0.0000	198.91	0.345
ΣPCDD/PCDF	1305	1.05	0.0067	1638.1	2.312
I-TEQ (PCDD/DF)	46.9 ± 22.5	0.0511	0.0016	111.39	0.086

Ref.1- Abad et al. (2006); Ref.2 -Chen et al. (2008); Ref.3- Lee et al. (2007); Ref.4- Meneses et al (2004);

\*-average value ± standard deviation.

Table 10. Concentration of PCDD/PCDF in air emissions from MSWI.

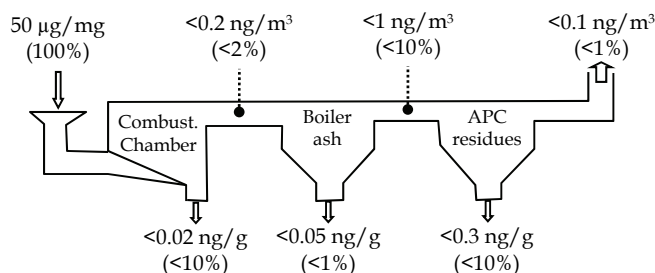


Fig. 10. PCDD/PCDF mass balance in modern MSW incinerator plant (adapted from McKay, 2002).

and lipid metabolism, changes in activities of various liver enzymes, depression of the immune system, and endocrine and nervous system abnormalities. It is a potent teratogenic and fetotoxic chemical in animals (Mukerjee, 1998). Indeed, 2,3,7,8-TCDD seems to be a very potent promoter of carcinogenesis in liver of rat, and populations occupationally exposed to dioxins have increased incidences of soft-tissue sarcoma and non-Hodgkin's lymphoma.

Fig. 10 shows a representative mass balance in a modern MSWI unit, where it is implicit that overall the incineration process is now a sink of dioxins. In general, if high technology combustion is combined with sophisticated APC devices an emission factor of 0.5  $\mu\text{g}$  I-TEQ/ton of MSW can be assumed to air, 15  $\mu\text{g}$  I-TEQ/ton to fly ashes and 1.5  $\mu\text{g}$  I-TEQ/ton to bottom ashes (UNEP, 2005).

At the end, it is very important to note that the 2,3,7,8-TCDD concentration in human tissue is decreasing by about a factor of 7 over a 25-year period (Hites, 2011).

#### 4.11 Green house gases

Green house gases enclose carbon dioxide ( $\text{CO}_2$ ), methane ( $\text{CH}_4$ ), nitrous oxide ( $\text{N}_2\text{O}$ ), hydrofluorocarbons (HFC) perfluorocarbons (PFC) and sulphur hexafluoride ( $\text{SF}_6$ ). Specific emissions of  $\text{CO}_2$  usually observed in MSWI are in the range of 0.1 to 1.7 ton/ton of MSW. The organic compounds of MSW are biomass and fossil wastes, and so the fraction of  $\text{CO}_2$  from fossil must be taken into account for the climate changes. Concerning methane, since the furnace is kept at high oxidative conditions, no emissions of  $\text{CH}_4$  are expected in stack gases. Some methane can be formed during long periods of waste storage and under anaerobic conditions. In the cases where primary air is supplied from the storage bunker, the  $\text{CH}_4$  is oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

In Table 11 a summary of the most important techniques/technologies is indicated for the reduction of the main incineration pollutant described above (BREF, 2006).

### 5. The impact on health of emissions to air from MSWI

The activity of MSW incineration may pose environmental problems at various levels, concerning either ambient contamination provoked mainly by gaseous emissions or coming from the landfilling of APC residues after being submitted to solidification/stabilization treatment. Highly toxic PCDD/PCDF or harmful heavy metals such as Cd, Pb and Cr can be spread in the surroundings of incinerators plants and landfill disposal facilities. Ultimately, population health living nearby may be adversely affected by carcinogenic and non-carcinogenic compounds so that assessing their risk on the potential increase of human diseases is truly advisable. In this ambit some literature studies have addressed this theme.

Cangialosi et al. (2008) described the health impact associated to the gaseous emissions of a municipal solid waste incinerator in Italy, based on an atmospheric dispersion model involving pollutants content and human exposure level. Food intake revealed to be the major threat when compared with air inhalation and dermal contact, being, however, the carcinogenic (dioxins, furans, Cd) and non-carcinogenic (Pb and Hg) contamination values lower than those accepted. Therefore, their final conclusions supported that no relevant health problems may be endorsed to modern MSWI systems. Volatile organic compounds and bioaerosols possibly attributed to a MSWI plant in Spain (Vilavert et al., 2011) were checked and potential risks for human health were not identified once pollutants concentrations were similar to those observed in other regions. In a comparative study, Moy et al. (2008) reported that the landfill impact in human health through inhalation is five times higher than the one associated to the incineration operation, with cancer risk for both alternatives considered as acceptable when analysing data from New York City, whereas non-cancer health problems showed to be unacceptable. Concerning landfill sites for disposal of air pollution control (APC) residues from municipal solid wastes in UK, health risks for direct and indirect human exposure were also assessed with dispersion models by

Macleod et al. (2006) revealing that irrelevant danger was associated to inhalation while tolerable daily soil intake (TDSI) could be possibly surpassed due to the high deposition levels of those residues. Investigations about the impact of harmful PCDD/PCDF released

Pollutant	Techniques
Particles	Electrostatic precipitators Wet electrostatic precipitators Condensation electrostatic precipitators Ionization wet scrubbers Fabric filters Cyclones and multi-cyclones
Acid gases (HCl, HF, SO <sub>x</sub> , ...)	Wet-scrubber Semi-dry scrubber (e.g. suspension of lime) + bag filter Dry-scrubber (e.g. lime or sodium bicarbonate)
Direct desulphurisation	Injection of adsorbents (e.g. calcium compounds) directly into the incineration chamber
Oxides of nitrogen (NO <sub>x</sub> )	Primary techniques: air and temperature control, flue-gas recirculation, Secondary techniques: Selective Non- Catalytic Reduction (SNCR) and Selective Catalytic Reduction (SCR).
Hg	Primary techniques: separate collection, restrictions of receipt contaminated wastes Secondary techniques: scrubber by adding oxidants, activated carbon, furnace coke or zeolites
Other heavy metals	Converted into no-volatile oxides and deposited into fly ash, all techniques referred to remove particles can be applied. Activated carbon injection into scrubbing units.
Organic carbon compounds	Adsorption on activated carbon. SCR used for NO <sub>x</sub> . Catalytic bag filters Static bed filters Rapid quenching of flue-gas
Greenhouse gases (CO <sub>2</sub> , N <sub>2</sub> O)	All techniques used for NO <sub>x</sub> . Increase energy recovery efficiency
APC residues	Treated (e.g. solidification/stabilization and disposed of) Thermal treatment (vitrification, melting, sintering) Extraction and separation Chemical stabilisation
Bottom ash	Separation of metals Screening and crushing Treatment using ageing conditions High temperature slagging rotary kilns

Table 11. Most important techniques for the reduction of the main incinerator pollutants.



from a MSWI in Korea (Oh et al., 2006) showed that those emissions affected more directly atmosphere quality, with furan levels in air closer to the emitted values than those found in soil. In order to deepen consequences of environment contamination of MSWI, Cordier et al. (2004) analysed birth malformations in the population surrounding 70 incinerators in France. Though congenital problems were not significantly more relevant in those groups, higher incidence of some anomalies associated to renal, urology, cardiology and skin pathologies could be ascertained to persistent pollutants accumulated from the old incineration methodologies and road traffic pollution as well. The effect resulting from the application of more restrictive environment EU legislation regarding MSWI emissions was considered by Meneses et al. (2004), by determining PCDD/Fs concentrations in air, soil and vegetation, and their danger for human health, having concluded that both pollutants emissions and cancer risk was reduced after those measures implementation. Other contamination sources were, nevertheless, pointed out since pollutants emission levels diminished more significantly than health problems after the installation of new cleaning gas systems. Also, the replacement of old systems (electrostatic precipitator) by new technologies (semi-dry scrubber, fabric filters and charcoal injection) in Spain (Abad et al., 2003) revealed a significant decrease on dioxins emissions spread in stack gas, bottom ash and air pollution control residues, where the higher dioxin content was found. Heavy metal deposition around a MSWI area in USA showed quite different pollution concentrations during fall and winter (Feng et al., 2000). Methodologies envisaging minimisation of dioxins released from MSWI processes were reviewed by McKay (2002) accounting for three possible sources, furnace feedstock, precursor compounds or innocuous molecules forming dioxins by heterogeneous catalytic reactions or homogeneous thermal reactions. Finally, it is worthy to refer that in September 2009, the Health Protection Agency from UK analysed the on-going research about health impact of municipal solid waste incinerators and conclusions about the low influence in humans diseases of modern technologies were justified by the fact that emissions are nowadays well controlled, imparting, therefore, low contribution to global air pollution.

## 6. Conclusion

At present, municipal solid waste incineration (MSWI) in waste-to-energy (WtE) is considered to be an environmentally friendly technology, while allowing recovery of a large part of the energy enclosed in MSW. Indeed, MSWI is one of the main management options in most of the developed countries. Nonetheless, the main problems associated to these processes are the large volume of gaseous emissions which may pose environmental health risks (if not well cleaned) and the hazardous fly ash or air pollution control (APC) residues that remain after incineration. The main air pollution formed in MSWI that are nowadays under regulatory observation are: dust, CO, TOC, HCl, HF, SO<sub>2</sub>, NO<sub>x</sub>, Hg, Cd, Tl, Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V and PCDD/PCDF.

However, it is very important to note that air pollution induced by MSWI has been strongly reduced by some up-to-date sophisticated air pollution control equipments. In fact, process engineering of the gas cleaning systems can still be extended to lower emission limits if the environmental legislation so requires. It is only a question of overall cost of operation per ton of incoming waste to be incinerated.

Some studies that analysed in detail the health impact associated to the gaseous emissions of MSWI have revealed that no relevant health problems may be associated to modern MSWI systems.

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